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(54) Title: METHOD FOR PROTECTING AND/OR CONTROLLED RELEASE OF ACTIVE INGREDIENTS		
(57) Abstract <p>Use of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms as agent for the protection and/or controlled release of an active ingredient. Active ingredients suitable for protection and/or controlled release include bleaches and oxidants, bleach activators, bleach catalysts, photoactivators, fabric softening agents, perfumes, flavors, pigments, enzymes, vitamins, pharmaceuticals, antimicrobials, fertilizers, explosives, and corrosive materials. Preferably, the molecular sieve is a mesoporous molecular sieve consisting essentially of crystalline, inorganic material exhibiting after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least 18 Angstroms. The active ingredient is physically or chemically sorbed within the pores of the molecular sieve.</p>		

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## METHOD FOR PROTECTING AND/OR CONTROLLED RELEASE OF ACTIVE INGREDIENTS

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### TECHNICAL FIELD

The present invention relates to a compositions and methods for protecting environmentally-sensitive or hazardous active ingredients. The invention also relates to compositions and methods for the controlled-release of active ingredients in response to an external trigger.

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### BACKGROUND OF THE INVENTION

Effective protection and controlled release of active ingredients is an important objective in many consumer product applications designed for personal, household or institutional use. It is widely recognised, for example, that the function of detergency and other functional additives can be significantly impaired in detergent and related applications by interaction between the additive material and other components of the composition or even with environmental factors such as sunlight and air. For example, detergency enzymes can be deleteriously effected by interaction with bleaches, sequesterants, acids and bases, surfactants and air; perfumes, bleach activators and bleach catalysts can be deleteriously effected by interaction with bleaches; cationic surfactants can be deleteriously effected by interaction with anionic surfactants; fluorescers can be deleteriously effected by interaction with bleaches and cationic surfactants; and suds-suppressors can be deleteriously effected by interaction with surfactants. Moreover, the consumer acceptability of a product can also be significantly impaired as the result of physical interactions between an active ingredient and other components of a composition. For instance, a speckled detergent containing a water-soluble dye can lose its aesthetic appeal as a result of migration of the dye into the detergent base formula.

There are many other applications in which the protection of sensitive or hazardous active ingredients is of special importance. In the cosmetics and pharmaceutical fields, for example, product stability can often be impaired as a result of interactions between

incompatible actives or with environmental factors such as sunlight. Some vitamins, for example, are particularly prone to photo-induced degradation processes. There are also many active ingredients of a hazardous nature which require special measures for their safe storage, transportation and/or use. Corrosive materials, gases, and explosives all fall  
5 within this category.

Apart from the protection of sensitive ingredients, a great deal of research has also been made in the area of the controlled release of active ingredients such as drugs and agrichemicals. Controlled release technology, for example, offers many possibilities for  
10 new oral and parenteral dosage forms, e.g., for masking bitter tasting pharmaceuticals, providing extended release in vivo, or for providing enteric release of drugs. Broadscale consumer applications of controlled release technology outside the medical and agricultural fields are relatively limited at present, however, primarily for reasons of cost as well as technical deficiencies in current technology.

15 Accordingly, the present invention provides novel compositions and methods for protecting environmentally-sensitive or hazardous active ingredients and/or for the controlled release of active ingredients with improved technical performance and cost/benefit ratio.

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### SUMMARY OF THE INVENTION

In its broadest aspect, the present invention relates to the use of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms, preferably greater than  
25 about 10 Angstroms, as agent for the protection and/or controlled release of an active ingredient.

Preferred molecular sieves herein are selected from:

- a) mesoporous molecular sieves having a pore diameter of at least 13, preferably at least  
30 15, and more preferably at least 20 Angstroms;
- b) phosphate-containing molecular sieves, especially those selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn; and
- 35 c) mixtures thereof.

Of these, highly preferred are the mesoporous molecular sieves designated M41S which consist essentially of crystalline, inorganic material exhibiting after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least 18 Angstroms. A highly preferred material under the M41S designation is MCM-41 which can be described  
5 as a mesoporous molecular sieve consisting essentially of inorganic, porous, crystalline material having, after calcination, a hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units.

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In a method aspect, the present invention provides a method of protecting an environmentally-sensitive or hazardous active ingredient comprising physically or chemically sorbing the ingredient within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms.

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In another method aspect, the invention provides a method for the controlled release of an active ingredient comprising physically or chemically sorbing the ingredient within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms and releasing the ingredient under diffusion control or in response to an  
20 external trigger.

The nature of the external trigger will depend on the specific application. Examples of applications and corresponding triggers include:

<u>Application</u>	<u>Trigger</u>
Skin cosmetics	Perspiration, sunlight, air
Hair cosmetics	Sebum, sunlight, air
Oral compositions, toothbrushes	Saliva, mouth odors
Diapers, babywipes	Urine, faeces, body odors
Feminine protection products	Menses, body odors
Shoe inserts	Perspiration, body odor
Clothing, bedlinen	Perspiration
Pet treatment	Rainwater
Pet litter	Urine, faeces, pet odor
Wound dressings	Blood, wound excretion
Pharmaceuticals	pH, bacteria

The present invention also provides a composition comprising an environmentally-sensitive or hazardous active ingredient physically or chemically sorbed within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms.

- 5 Examples of environmentally-sensitive or hazardous ingredient include bleaches and oxidants, bleach activators, bleach catalysts, photoactivators, fabric softening agents, perfumes, flavors, pigments, enzymes, vitamins, skin/hair cosmetics, pharmaceuticals, antimicrobials, fertilizers, explosives, and corrosive materials.
- 10 In addition, such compositions will frequently comprise an antagonist for the environmentally-sensitive or hazardous ingredient. Examples of environmentally-sensitive ingredients and their specific antagonists include:

<u>Active Ingredient</u>	<u>Antagonist</u>
Detergency Enzymes	Bleaches, Sequesterants, Acids, Bases, Surfactants
Bleaches	Bleach Activators, Catalysts, Acids, Bases
Bleach Activators, Catalysts	Bleaches, Acids, Bases
Photoactivators, Dyes	Nonionic Surfactants
Suds Controllers	Surfactants
Fluorescers	Bleaches, Cationic Surfactants
Perfumes	Bleaches
Fabric Softening Agents	Anionic Surfactants

- In another composition aspect, there is provided a controlled-release composition
- 15 comprising an active ingredient physically or chemically sorbed within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms and being releasable therefrom by diffusion control or in response to an external trigger.

- 20 Examples of active ingredients suitable for controlled release include bleaches and oxidants, bleach activators, bleach catalysts, photoactivators, fabric softening agents, perfumes, flavors, pigments, enzymes, vitamins, skin/hair cosmetics, pharmaceuticals, antimicrobials, fertilizers, explosives, and corrosive materials.

The compositions herein can take various forms including optionally agglomerated particulate solids, membranes, encapsulates, bars, liquids, gels and aerosols.

- 5 The present invention also provides a variety of consumer and retail products designed for personal, household, industrial and institutional use.

### **DETAILED DESCRIPTION OF THE INVENTION**

10 The compositions herein comprise a large pore molecular sieve in an amount effective for protecting and/or controlling the release of an active ingredient, preferably in an amount of at least about 0.001%, more preferably from about 0.001% to about 20%, and most preferably from about 0.05% to about 10% by weight of composition.

15 As used herein, the term "large pore molecular sieve" refers to a range of microporous and mesoporous crystalline materials built around an inorganic charged or neutral framework and possessing pores having a relatively uniform size distribution. In general, the pore diameter of the molecular sieves herein should be greater than about 8 Angstroms. Preferred herein, however, are molecular sieves falling within the class of mesoporous materials wherein the pore diameter is preferably at least about 13, more preferably at  
20 least about 15 and especially at least about 20 Angstroms. Mesoporous molecular sieves of this type can be generally described as crystalline, inorganic materials which exhibit after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least about 18 Angstroms. As used herein, the term 'crystalline' indicates that the molecular sieve has sufficient order to provide, following calcination, a diffraction pattern  
25 such as, for example, by X-ray, electron or neutron diffraction with at least one peak. It should also be noted that the molecular sieve may exist as a mixture of physically distinct phases. Also, defects and imperfections can cause significant deviations from an ideal regular structure. Generally, however, the pore size distribution within a single phase will be within about 25%, usually within about 15% of the average pore size for that phase.

30 The pore diameter of the molecular sieves can be determined in known manner, for example, by transmission electron microscopy (TEM), x-ray diffraction or argon physisorption. TEM is the preferred technique herein. Suitable methods for determining pore diameter by argon physisorption are disclosed in US-A-5,098,684.

Molecular sieves suitable for use herein include large pore natural and synthetic zeolites, i.e., molecular sieves based on a crystalline silicate or aluminosilicate framework, as well as phosphate-containing molecular sieves and zeolite analogs such as aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element such as Mg, Ti, Mn, Co, Fe, Ga, or Zn. Large pore silicate molecular sieves (essentially aluminium-free) are also suitable for use herein. For a general discussion of zeolite-type molecular sieves, see D.W. Breck, *Zeolite Molecular Sieves, Structure, Chemistry and Use*, John Wiley & Sons, Inc., New York, 1974.

Molecular-sieves of the aluminosilicate variety (zeolites) can be represented by the empirical formula  $M_{2/n}O \cdot Al_2O_3 \cdot ySiO_2 \cdot wH_2O$ , where y is 2 or greater, M is the charge balancing cation, such as sodium, potassium, ammonium, magnesium, and calcium, n is the cation valence, and w represents the moles of water contained in the zeolitic voids.

The zeolite framework is made up of  $SiO_4$  tetrahedra linked together by sharing of oxygen ions. Substitution of a Group IIIB metal such as Al for Si generates a charge imbalance, necessitating the inclusion of a cation. The structures contain channels or interconnected voids that are occupied by the cations and water molecules. The water may be removed reversibly, generally by the application of heat, which leaves intact the crystalline host structure permeated with micropores that may account for >50% of the microcrystal's volume. In some zeolites, dehydration may produce some perturbation of the structure, such as cation movement, and some degree of framework distortion.

There are two basic types of zeolite structures: one provides an internal pore system comprising interconnected cage-like voids; the second provides a system of uniform channels which, in some instances, are one-dimensional and in others intersect with similar channels to produce two- or three-dimensional channel systems. The preferred type has two- or three-dimensional channel systems to provide rapid intracrystalline diffusion in adsorption and catalytic applications.

Substitution of phosphorus for some or all of the framework silicon not only makes it possible to extend the range of molecular sieves to higher pore sizes but it also has significant impact on the residual framework charge, hydrophobicity, and the binding/complexing character of the molecular sieve.



Molecular sieves of the phosphate-containing class are well-known and are disclosed in a number of documents. Suitable aluminophosphates, for example, include those disclosed in US-A-4,310,440 and US-A-4,385,994. These aluminophosphates have essentially electroneutral lattices. US-A-3,801,704 discloses an aluminophosphate treated in a certain way to impart acidity.

An early reference to a hydrated aluminophosphate which is crystalline until heated at about 110 °C., at which point it becomes amorphous or transforms, is the "H<sub>1</sub>" phase or hydrate of aluminium phosphate of F. d'Yvoire, Memoir Presented to the Chemical Society, No. 392, "Study of Aluminium Phosphate and Trivalent Iron", July 6, 1961 (received), pp.1762-1776. This material, when crystalline, is identified by the JCPDS Internal Center for Diffraction Data card number 15-274. Once heated at about 110 °C., however, the d'Yvoire material becomes amorphous or transforms to the aluminophosphate form of tridymite.

Compositions comprising crystals having a framework topology after heating at 110 °C or higher giving an X-ray diffraction pattern consistent with a material having pore windows formed by 18 tetrahedral members of about 12-13 Angstroms in diameter are disclosed in US-A-No. 4,880,611.

A naturally occurring, highly hydrated basic ferric oxyphosphate mineral, cacoxenite, is reported by Moore and Shen, Nature, Vol. 306, No. 5941, pp. 356-358 (1983) to have a framework structure containing very large channels with a calculated free pore diameter of 14.2 Angstroms.

Silicoaluminophosphates of various structures are disclosed in US-A-4,440,871, US-A-3,355,246 (ZK-21) and US-A-3,791,964 (ZK-22). Other disclosures of silicoaluminophosphates and their synthesis include US-A-4,673,559 (two-phase synthesis method); US-A-4,623,527 (MCM 10); US-A-4,639,358 (MCM-1); US-A-4,647,442 (MCM-2); US-A-4,664,597 (MCM-4); US-A-4,638,357 (MCM-5); and US-A-4,632,811 (MCM-3).

A method for synthesizing crystalline metalloaluminophosphates is disclosed in US-A-4,713,227, while an antimonophosphoaluminate and its synthesis are disclosed in US-A-4,619,818. US-A-4,567,029 discloses metalloaluminophosphates, while titaniumaluminophosphate and its synthesis are disclosed in US-A-4,500,651.

Other suitable phosphate-containing molecular sieves include the phosphorus substituted zeolites of CA-A-911,416; CA-A-911,417; and CA-A-911,418.

US-A-4,363,748 describes a combination of silica and aluminium-calcium-cerium phosphate as a low acid activity catalyst for oxidative dehydrogenation. GB-A-2,068,253 discloses a combination of silica and aluminium-calcium-tungsten phosphate as a low acid activity catalyst for oxidative dehydrogenation. US-A-4,228,036 discloses an alumina-aluminium phosphate-silica matrix as an amorphous body to be mixed with zeolite for use as cracking catalyst. US-A-3,213,035 teaches improving hardness of aluminosilicate catalysts by treatment with phosphoric acid. The catalysts are amorphous.

Other patents teaching aluminophosphates include US-A-4,365,095; US-A-4,361,705; US-A- US-A-4,222,896; US-A-4,210,560; US-A-4,179,358; US-A-4,158,621; US-A-4,071,471; US-A-4,014,945; US-A-3,904,550; and US-A-3,697,550.

Other pertinent references on phosphate-containing molecular sieves include S.T. Wilson and co-workers, J. Amer. Chem. Soc. 104, 1146 (1982); S.T. Wilson, B.M. Lok, C.A. Messina, and E.M. Flanigen, ACS Symp. Ser. 218,79 (1983); B.M. Lok and co-workers, J. Amer. Chem. Soc. 106, 6092 (1984); U.S. Pat. 4,554,143; U.S. Pat. 4,567, 029 S.T. Wilson and E.M. Flanigen, ACS Symp. Ser. 398,329 (1989); and E.M. Flanigen, B.M. Lok, R.L. Patton, and S.T. Wilson, Pure & Appl.Chem.58,1351 (1986).

A number of specific synthetic routes to large pore phosphate-containing molecular sieves have been reported in the literature, for example,  $\text{AlPO}_4\text{-8}$  ( R.M. Dessau, J.L. Schlenker, and J.B. Higgins, Zeolites 10,522 (1990)); VPI-5 ( M.E. Davis, C. Montes, and J.M. Garces, ACS Symp. Ser. 398, 291 (1989)); cloverite (J. Patarin and co-workers, Proc. 9<sup>th</sup> Intern. Zeolite Conf. I, 263 (1993)); and JDF-20 (Q. Huo and co-workers, J. Chem. Soc., Chem. Commun. 875 (1992)). Cacoenite, a natural large pore ferroaluminophosphate has also been structurally characterised (P.B. Moore and J. Shen, Nature 306, 356 (1983)).

Of all the above, molecular sieves of the phosphate-containing type preferred for use herein include  $\text{AlPO}_4\text{-5}$ ,  $\text{AlPO}_4\text{-8}$ , SAPO-5, SAPO-37, VPI-5, Cloverite (an 18-membered ring gallophosphate), and JDF-20.

Another class of large pore molecular sieves suitable for use herein are the liquid crystal template-synthesised M41S range of mesoporous molecular sieves reported by C.T.

Kresge and co-workers, Nature 359, 710 (1992) and by Beck and co-workers, J. Amer. Chem. Soc. 114, 10834 (1992). See also US-A-5,102,643, US-A-5,250,282, US-A-5,264,203, US-A-5,145,816, US-A-5,098,684, US-A-5,378,440, US-A-5,098,684, US-A-5,108,725 and US-A-5,057,296.

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In general terms, the M41S mesoporous molecular sieves can be described (see US-A-5,378,440) as inorganic, porous, non-layered crystalline phase materials which exhibit, after calcination, an X-ray diffraction pattern with at least one peak at a d-spacing greater than about 18 Angstrom Units with a relative intensity of 100 and a benzene adsorption  
10 capacity of greater than 15 grams benzene per 100 grams of anhydrous crystal at 50 torr and 25 °C.

Highly preferred M41S molecular sieves herein are mesoporous molecular sieves which consist essentially of inorganic, porous, crystalline material having, after calcination, a  
15 hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units. Such materials have been given the designation MCM-41 (see US-A-5,378,440).

20 Preferred large pore molecular sieves for use herein have a pore diameter of about 13 Angstroms or greater, more preferably of about 20-200 Angstroms, and most preferably about 30-100 Angstroms. Also preferred molecular sieves herein have surface area of at least about 300 m<sup>2</sup>/g, more preferably at least about 400 m<sup>2</sup>/g and most preferred being at least about 500 m<sup>2</sup>/g. In addition, the molecular sieves preferred for use herein are  
25 relatively hydrophobic, being either aluminium-free or having an Si:Al molar ratio of at least about 10:1, preferably at least about 30:1, more preferably at least about 60:1, and especially at least about 100:1

The molecular sieves can be used in colloidal or micron-sized form (with a primary  
30 particle size of less than about 10 microns, preferably less than about 1 micron, more preferably less than about 0.1 micron) or they can be used as larger sized particles (compositions at risk of inhalation, for example, will generally have a particle size in excess of 10 microns, preferably greater than 15 microns) or they can be shaped or agglomerated into a wide variety of particle sizes. Generally speaking,  
35 shaped/agglomerated particles can be in the form of a powder, a granule, or a molded product, such as an extrudate having particle size sufficient to pass through a 2 mesh

(Tyler) screen and be retained on a 400 mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion, the molecular sieve can be extruded before drying or partially dried and then extruded.

- 5 It may be desirable to incorporate the molecular sieves with a binder or a porous matrix material. Suitable binders include inorganic materials such as sodium sulphate, clays, silica and/or metal oxides, such as alumina, titania, and/or zirconia. The latter may be either naturally occurring or in the form of gelatinous precipitates or gels, including mixtures of silica and metal oxides. The clays may be naturally occurring clays, e.g.,  
10 bentonite and kaolin. Suitable organic binders include cellulose derivatives such as carboxymethyl cellulose and water-soluble polymers such as sodium polyacrylate. Porous matrix suitable herein include silica-alumina, silica-magnesia, silica zirconia, silica-thoria, silica-beryllia, silica-titania as well as ternary compositions such as silica-alumina-thoria, silica-alumina-zirconia, silica-alumina-magnesia and silica-magnesia-zirconia.

- 15 The active ingredient can be introduced into the pores of the molecular sieve in a number of ways, for example, by incipient wetness impregnation. In a preferred method, the molecular sieve is contacted with the active ingredient in liquid or gaseous form or, in the case of solid active ingredients, the molecular sieve is contacted with a solution or  
20 colloidal dispersion of the active ingredient. The active ingredient will generally be incorporated in the molecular sieve at a weight ratio (active ingredient:sieve) in the range from about 1:1000 to about 10:1, preferably from about 1:100 to about 1:1, more preferably from about 1:20 to about 1:4.

- 25 Preferred active ingredients for incorporation within the molecular sieve include:

a) Bleaches and oxidants

Suitable bleaching agents herein include chlorine and oxygen-releasing bleaching agents inclusive of hydrogen peroxide, inorganic perhydrates and organic peroxy acids.

- 30 Examples of inorganic perhydrate salts include perborate, percarbonate, perphosphate, persulfate and persilicate salts. The inorganic perhydrate salts are normally the alkali metal salts.

- Sodium perborate can be in the form of the monohydrate of nominal formula  
35  $\text{NaBO}_2\text{H}_2\text{O}_2$  or the tetrahydrate  $\text{NaBO}_2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ . Alkali metal percarbonates, particularly sodium percarbonate are preferred perhydrates for inclusion herein. Sodium

percarbonate is an addition compound having a formula corresponding to  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , and is available commercially as a crystalline solid. Potassium peroxymonopersulfate is another inorganic perhydrate salt of utility herein.

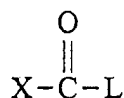
- 5 Organic peroxy acids suitable for use herein include aryl peroxyacids such as perbenzoic acid, alkyl peroxyacids such as peracetic acid and pernonanoic acid, cationic peroxyacids, etc, and amide-substituted peroxy acids (see EP-A-0170386). Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioc acid, diperoxytetradecanedioc acid, and diperoxyhexadecanedioc acid. Dibenzoyl peroxide is a  
10 preferred organic peroxyacid herein. Mono- and diperazelaic acid, mono- and diperbrassylic acid, and N-phthaloylaminoperoxycaproic acid are also suitable herein.

Other oxidants suitable for use as the active ingredient herein include ammonium nitrate, sodium nitrate, sodium chlorate and calcium nitrate.

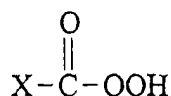
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#### b) Bleach Activators

- Bleach activators can generally be described as organic peroxyacid bleach precursors, i.e., compounds that react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid, e.g. aryl peroxyacids such as perbenzoic acid, alkyl peroxyacids such as  
20 peracetic acid and pernonanoic acid, amide substituted alkyl peroxyacids, cationic peroxyacids, etc. Generally peroxyacid bleach precursors may be represented as



- 25 where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



- 30 Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, GB-A-864798, GB-A-1147871,

GB-A-2143231 and EP-A-0170386. Cationic peroxyacid precursors are described in US-A-4,904,406; US-A-4,751,015; US-A-4,988,451; US-A-4,397,757; US-A-5,269,962; US-A-5,127,852; US-A-5,093,022; US-A-5,106,528; GB-A-1,382,594; EP-A-0475512, EP-A-0458396 and EP-A-0284292; and in JP87-318,332.

5

#### c) Bleach Catalysts

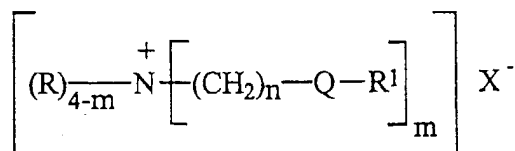
Bleach catalysts suitable as the active ingredient herein include the manganese triazacyclononane and related complexes (US-A-4246612, US-A-5227084); Co, Cu, Mn  
10 and Fe bispyridylamine and related complexes (US-A-5114611); and pentamine acetate cobalt(III) and related complexes(US-A-4810410).

#### d) Fabric Softening Agents

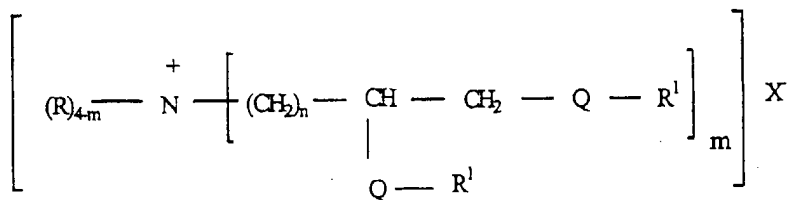
The fabric softening agent (sometimes referred to herein as the softener active) is  
15 preferably selected from cationic, nonionic, amphoteric and anionic fabric softening agents and mixtures thereof. Typical of the cationic softening agents are the quaternary ammonium compounds or amine precursors thereof as defined hereinafter.

Preferred quaternary ammonium fabric softening compounds have the formula

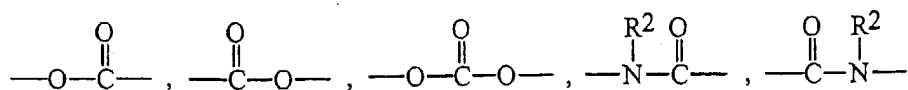
20



or the formula:



25 wherein Q is a carbonyl unit having the formula:



each R unit is independently hydrogen, C<sub>1</sub>-C<sub>6</sub> alkyl, C<sub>1</sub>-C<sub>6</sub> hydroxyalkyl, and mixtures thereof, preferably methyl or hydroxy alkyl; each R<sup>1</sup> unit is independently linear or

branched  $C_{11}$ - $C_{22}$  alkyl, linear or branched  $C_{11}$ - $C_{22}$  alkenyl, and mixtures thereof,  $R^2$  is hydrogen,  $C_1$ - $C_4$  alkyl,  $C_1$ - $C_4$  hydroxyalkyl, and mixtures thereof; X is an anion which is compatible with fabric softener actives and adjunct ingredients; the index m is from 1 to 4, preferably 2; the index n is from 1 to 4, preferably 2.

- 5 Of these, preferred are the Diester and/or Diamide Quaternary Ammonium (DEQA) compounds, in which Q is  $-O_2C-$  and  $-NR^2CO-$  respectively, preferred DEQA compounds being prepared by acylation of an amine such as methyl bis(2-hydroxyethyl)amine, methyl bis(2-hydroxypropyl)amine, methyl (3-aminopropyl) (2-hydroxyethyl)amine, methyl bis(2-aminoethyl)amine, triethanolamine or di(2-aminoethyl)ethanolamine,  
10 followed by quaternisation.

- An example of a preferred fabric softener active is a mixture of DEQA quaternized amines wherein R is methyl;  $R^1$  is a linear or branched alkyl or alkenyl chain comprising at least 11 atoms, preferably at least 15 atoms, m is 2, and  $QR^1$  represents a fatty acyl unit  
15 ( $O_2CR^1$ ) which is typically derived from a triglyceride source such as tallow, partially hydrogenated tallow, lard, partially hydrogenated lard, vegetable oils and/or partially hydrogenated vegetable oils, such as, canola oil, safflower oil, peanut oil, sunflower oil, corn oil, soybean oil, tall oil, rice bran oil, etc. and mixtures of these oils.

- 20 Examples of quaternary ammonium softening compounds include methylbis(tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate and methylbis(hydrogenated tallowamidoethyl)(2-hydroxyethyl)ammonium methylsulfate; these materials are available from Witco Chemical Company under the trade names Varisoft® 222 and Varisoft® 110, respectively, and N,N-di(tallowoyl-oxy-ethyl)-N,N-  
25 dimethyl ammonium chloride, where the tallow chains are at least partially unsaturated (Iodine Value (IV) of the corresponding fatty acid in the range of from 5 to 100).

- Other suitable quaternary ammonium fabric softening compounds for use herein are cationic nitrogenous salts having two or more long chain acyclic aliphatic  $C_8$ - $C_{22}$   
30 hydrocarbon groups or one said group and an arylalkyl group which can be used either alone or as part of a mixture, for example diamino alkoxyated quaternary ammonium salts and dialkyldimethylammonium salts such as ditallowdimethylammonium chloride, ditallowdimethylammonium methylsulfate, di(hydrogenatedtallow)dimethylammonium chloride, distearyldimethylammonium chloride, and dibehenyldimethylammonium  
35 chloride.

Suitable amine fabric softening compounds for use herein, which may be in amine form or cationic form are selected from reaction products of higher fatty acids with a polyamine selected from hydroxyalkylalkylenediamines and dialkylenetriamines (e.g., diethylenetriamine) and mixtures thereof. Preferred compounds of this type are

5 substituted imidazoline compounds, for example Mazamide® 6, sold by Mazer Chemicals, or Ceranine® HC, sold by Sandoz Colors & Chemicals; stearic hydroxyethyl imidazoline sold under the trade names of Alkazine® ST by Alkaril Chemicals, Inc., or Schercozoline® S by Scher Chemicals, Inc.; N,N"-ditallowalkoyldiethylenetriamine; 1-tallowamidoethyl-2-tallowimidazoline; and methyl-1-tallowamidoethyl-2-

10 tallowimidazolinium methylsulfate sold by Witco Chemical Company under the tradename Varisoft® 475. Other suitable substituted imidazoline fabric softening compounds include 1-oleylamidoethyl-2-oleylimidazolinium chloride.

Nonionic fabric softening compounds suitable for use herein, especially in dryer-added

15 embodiments, typically have an HLB of from about 2 to about 9, preferably from about 3 to about 7 and are relatively crystalline and higher melting (e.g., >25°C.) The level of nonionic softener is typically from about 10% to about 50%, preferably from about 15% to about 40%.

20 Preferred nonionic softeners are fatty acid partial esters of polyhydric alcohols, or anhydrides thereof, wherein the alcohol, or anhydride, contains from about 2 to about 18, preferably from about 2 to about 8, carbon atoms, and each fatty acid moiety contains from about 8 to about 30, preferably from about 16 to about 20, carbon atoms. Typical examples

25 of said fatty acids being lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and behenic acid. Typically, such softeners contain from about 1 to about 4, preferably about 2 fatty acid groups per molecule.

30 e) Perfumes and aromatherapy materials

Suitable perfumes are disclosed in U.S. Pat. 5,500,138. As used herein, perfume includes fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flowers, herbs, leaves, roots, barks, wood, blossoms or plants), artificial (i.e., a mixture of different nature oils or oil constituents) and synthetic (i.e., synthetically produced)

35 odoriferous substances. Such materials are often accompanied by auxiliary materials, such as fixatives, extenders, stabilizers and solvents. These auxiliaries are also included within



the meaning of "perfume", as used herein. Typically, perfumes are complex mixtures of a plurality of organic compounds.

The range of the natural raw substances can embrace not only readily-volatile, but also moderately-volatile and slightly-volatile components and that of the synthetics can include representatives from practically all classes of fragrant substances, as will be evident from the following illustrative compilation: natural products, such as tree moss absolute, basil oil, citrus fruit oils (such as bergamot oil, mandarin oil, etc.), mastix absolute, myrtle oil, palmarosa oil, patchouli oil, petitgrain oil Paraguay, wormwood oil; alcohols, such as farnesol, geraniol, linalool, nerol, phenylethyl alcohol, rhodinol, cinnamic alcohol; aldehydes, such as citral, Helional™, alpha-hexyl-cinnamaldehyde, hydroxycitronellal, Lilial™ (p-tert-butyl-alpha-methyldihydrocinnamaldehyde), methylnonylacetaldehyde; ketones, such as allylionone, alpha-ionone, beta-ionone, isoraldein (isomethyl-alpha-ionone), methylionone; esters, such as allyl phenoxyacetate, benzyl salicylate, cinnamyl propionate, citronellyl acetate, citronellyl ethoxolate, decyl acetate, dimethylbenzylcarbinyl acetate, dimethylbenzylcarbinyl butyrate, ethyl acetoacetate, ethyl acetylacetate, hexenyl isobutyrate, linalyl acetate, methyl dihydrojasmonate, styrallyl acetate, vetiveryl acetate, etc.; lactones, such as gamma-undecalactone; various components often used in perfumery, such as musk ketone, indole, p-menthane-8-thiol-3-one, and methyl-eugenol; and acetals and ketals such as methyl and ethyl acetals and ketals, as well as acetals or ketals based on benzaldehyde, those comprising phenylethyl moieties, or more recently developed specialities such as acetals and ketals of oxo-tetralins and oxo-indanes (see US-A-5,084,440, issued January 28, 1992, assigned to Givaudan Corp).

Examples of other perfume materials suitable for use herein include geranyl acetate, dihydromyrcenyl acetate, terpinyl acetate, tricyclodecenyl acetate, tricyclodecenyl propionate, 2-phenylethyl acetate, benzyl acetate, benzyl benzoate, styrallyl acetate, amyl salicylate, phenoxyethyl isobutyrate, neryl acetate, trichloromethyl-phenylcarbinyl acetate, p-tertiary butyl-cyclohexyl acetate, isononyl acetate, cedryl acetate, benzyl alcohol, tetrahydrolinalool, citronellol, dimethylbenzylcarbinol, dihydromyrcenol, tetrahydromyrcenol, terpineol, eugenol, vetiverol, 3-isocamphyl-cyclohexanol, 2-methyl-3-(p-tertiary butylphenyl)-propanol, 2-methyl-3-(p-isopropylphenyl)-propanol, 3-(p-tertiary butylphenyl)-propanol, alpha-n-amylocinnamic aldehyde, 4-(4-hydroxy-4-methylpentyl)-3-cyclohexenecarbaldehyde, 4-(4-methyl-3-pentenyl)-3-cyclohexenecarbaldehyde, 4-acetoxy-3-pentyl-tetrahydropyran, 2-n-heptyl-

cyclopentanone, 3-methyl-2-pentyl-cyclopentanone, n-decanal, n-dodecanal, hydroxycitronellal, phenylacetaldehyde dimethyl acetal, phenylacetaldehyde diethyl acetal, geranonitrile, citronellonitrile, cedryl methyl ether, isolongifolanone, aubepine nitrile, aubepine, heliotropine, coumarin, vanillin, diphenyl oxide, ionones, methyl  
5 ionones, isomethyl ionones, irones, cis-3-hexenol and esters thereof, indane musks, tetralin musks, isochroman musks, macrocyclic ketones, macrolactone musks, ethylene brassylate, aromatic nitromusks and mixtures thereof.

#### f) Flavors

- 10 Flavorants suitable for use as the active ingredient herein include wintergreen oil, oregano oil, bay leaf oil, peppermint oil, spearmint oil, clove oil, sage oil, sassafras oil, lemon oil, orange oil, anise oil, benzaldehyde, bitter almond oil, camphor, cedar leaf oil, marjoram oil, citronella oil, lavender oil, mustard oil, pine oil, pine needle oil, rosemary oil, thyme oil, cinnamon leaf oil, and mixtures thereof.

15

#### g) Pigments

- Pigments suitable for use as the active ingredient can be organic and/or inorganic. Also included within the term pigment are materials having a low colour or lustre such as matte finishing agents, and also light scattering agents. Examples of suitable pigments are iron oxides,  
20 acyglutamate iron oxides, ultramarine blue, D&C dyes, carmine, and mixtures thereof. The pigments can be treated with compounds such as amino acids, silicones, lecithin and ester oils.

#### h) Enzymes

- 25 Enzymes suitable herein include bacterial and fungal cellulases such as Carezyme and Celluzyne (Novo Nordisk A/S); peroxidases; lipases such as Amano-P (Amano Pharmaceutical Co.), M1 Lipase<sup>R</sup> and Lipomax<sup>R</sup> (Gist-Brocades) and Lipolase<sup>R</sup> and Lipolase Ultra<sup>R</sup> (Novo); cutinases; proteases such as Esperase<sup>R</sup>, Alcalase<sup>R</sup>, Durazym<sup>R</sup> and Savinase<sup>R</sup> (Novo) and Maxatase<sup>R</sup>, Maxacal<sup>R</sup>, Properase<sup>R</sup> and Maxapem<sup>R</sup> (Gist-Brocades);  
30 and  $\alpha$  and  $\beta$  amylases such as Purafect Ox Am<sup>R</sup> (Genencor) and Termamyl<sup>R</sup>, Ban<sup>R</sup>, Fungamyl<sup>R</sup>, Duramyl<sup>R</sup>, and Natalase<sup>R</sup> (Novo); and mixtures thereof.

#### i) Skin/Hair Cosmetics

- 35 Skin/hair cosmetics suitable for use as the active ingredient herein include vitamins and various lipophilic or hydrophobic materials having a moisturising or emollient function

including liquids, gels, waxes, particulate solids, etc. Suitable hydrophobic materials and emollients include fatty acids such as lauric and oleic acid, fatty alcohol esters such as isopropyl myristate and isopropyl palmitate, water-insoluble ethers and alcohols such as lauryl alcohol, hexadecyl alcohol, and oleyl alcohol, paraffins and mineral oils,  
5 polyorgano silicones and mixtures thereof. Such materials are disclosed in US-A-4,053,851, US-A-4,065,564, US-A-4,073,880, US-A-4,278,655, and GB-A-2,018,590.

Preferred hydrophobic materials include volatile silicone oils. As used herein, "volatile" refers to those materials which have a measurable vapor pressure at ambient conditions.  
10 Such volatile silicone oils may be cyclic or linear. A description of volatile silicone oils is found in Todd, et al., "Volatile Silicone Fluids for Cosmetics", 91 Cosmetics and Toiletries, 27-32 (1976). Preferred volatile silicone oils include those having from about 3 to about 9 silicon atoms, preferably containing from about 4 to about 5 silicon atoms. Examples include: Dow Corning 344, Dow Corning 345 and Dow Corning 200 (sold by  
15 Dow Corning Corporation); 7207 and 7158 (sold by General Electric Company); and SWS-03314 (sold by SWS Silicones Corporation).

Preferred skin/hair cosmetics for use herein include vitamins and other cosmetic actives which are known to be sensitive to oxidative degradation such as vitamin A and vitamin  
20 E. The actives are introduced into the molecular sieve by, for example, incipient wetness impregnation in an organic solvent phase. The molecular sieve is then incorporated in a skin cosmetic such as a sunscreen, anti-UV cream or other cosmetic emulsion, the active ingredient being releasable therefrom in response to an external trigger such as perspiration.

25 Other active ingredients suitable for incorporation in the molecular sieve include suds-suppressors, especially materials of the silicone, wax, vegetable and hydrocarbon oil and phosphate ester varieties; fluorescers such as Blankophor MBBH and Tinopal CBS and EMS; photoactivators such as zinc phthalocyanine tri- and tetrasulphonates;  
30 pharmaceuticals e.g. actives targeted for release in the lower gastrointestinal tract or for intranasal release; fertilizers such as ammonium nitrate; hazardous materials such as ammonia, fluorine, explosives, caustic alkalis, etc

The agents herein can be utilised in a wide variety of product applications, for example,  
35 detergent compositions for laundry, dishwashing or hard surface cleaning use; fabric conditioning compositions; perfume, odor-control and aromatherapy compositions; skin

and hair cosmetics such as sunscreens, anti-UV creams and the like; oral compositions inclusive of dentifrices, chewing gum and toothbrushes; pharmaceutical compositions for lower-GI and intranasal delivery; fertilizers, etc.

## Claims

- 5
1. Use of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms as agent for the protection and/or controlled release of an active ingredient.
  2. A method of protecting an environmentally-sensitive or hazardous active ingredient  
10 comprising physically or chemically sorbing the ingredient within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms.
  3. A method for the controlled release of an active ingredient comprising physically or  
15 chemically sorbing the ingredient within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms and releasing the ingredient under diffusion control or in response to an external trigger.
  4. A composition comprising an environmentally-sensitive or hazardous active ingredient  
20 physically or chemically sorbed within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms.
  5. A composition according to claim 4 wherein the environmentally-sensitive or hazardous ingredient is selected from bleaches and oxidants, bleach activators, bleach  
25 catalysts, photoactivators, fabric softening agents, perfumes, flavors, pigments, enzymes, vitamins, skin/hair cosmetics, pharmaceuticals, antimicrobials, fertilizers, explosives, corrosive materials, ...
  6. A composition according to claim 4 or 5 additionally comprising an antagonist for the  
30 environmentally-sensitive or hazardous ingredient.
  7. A controlled-release composition comprising an active ingredient physically or chemically sorbed within the pores of a large pore molecular sieve having a pore diameter greater than about 8 Angstroms and being releasable therefrom by diffusion control or in  
35 response to an external trigger.

8. A composition according to claim 7 wherein the active ingredient is selected from bleaches and oxidants, bleach activators, bleach catalysts, photoactivators, fabric softening agents, perfumes, flavors, pigments, enzymes, vitamins, skin/hair cosmetics, pharmaceuticals, antimicrobials, fertilizers, explosives, corrosive materials, ...
- 5 9. A composition according to any of claims 4 to 8 in the form of an optionally agglomerated particulate solid, membrane, encapsulate, bar, liquid, gel or aerosol.
- 10 10. A composition, method or use according to any preceding claim wherein the molecular sieve is selected from mesoporous molecular sieves having a pore diameter of at least 13, preferably at least 15, more preferably at least 20 Angstroms.
- 15 11. A composition, method or use according to claim 10 wherein the mesoporous molecular sieve consists essentially of crystalline, inorganic material exhibiting after calcination an X-ray diffraction pattern with at least one peak at a d-spacing of at least 18 Angstroms.
- 20 12 A composition, method or use according to claim 10 or 11 wherein the mesoporous molecular sieve consists essentially of inorganic, porous, crystalline material having, after calcination, a hexagonal arrangement of uniformly-sized pores having a pore diameter of at least about 13 Angstrom and exhibiting a hexagonal electron diffraction pattern that can be indexed with a  $d_{100}$  value greater than about 18 Angstrom units.
- 25 13 A composition, method or use according to any of claims 1 to 9 wherein the molecular sieve is a phosphate-containing molecular sieve, preferably selected from aluminophosphates, silicoaluminophosphates, metalloaluminophosphates and metallosilicoaluminophosphates wherein 'metallo' represents an additional metallic element selected from Mg, Ti, Mn, Co, Fe, Ga, and Zn.

# INTERNATIONAL SEARCH REPORT

Inter nal Application No

PCT/US 00/04908

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J20/02 B01J20/18 A61K7/46 A61K9/18 C11D17/00  
C11D3/12 C12N11/00 A01N25/08

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C11D A61K A01N C12N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

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